Electronic Supplementary Information

A general strategy for the production of photoluminescent carbon nitride dots from organic amine and their application as novel peroxidase-like catalysts to colorimetric detection of H_2O_2 and glucose

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Experimental section

Materials

3,3',5,5',-tetramethylbenzidine (TMB), acetic acid, dimethylamine (DIA), ethylamine (EA) and tripropylamine (TPA) were purchased from Aladin Ltd. (Shanghai, China). H_2SO_4, Na_2HPO_4, chlorosulfonic acid (CSA), HNO_3, sodium acetate (NaAc) and HCl were purchased from Beijing Chemical Corp. Glucose oxidase (GOD) was purchased from Aldrich Corp. All the chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of CNDs

The photoluminescent CNDs were prepared by microwave heating organic amine in the presence of acids. In a typical synthesis, 1 mL of H_2SO_4 was added into 5 mL of DIA solution. After that, the mixture was directly placed in a domestic microwave oven and irradiated at 700 W for 60 s. The excess precursors and resulting small molecules were removed by dialyzing against water through a dialysis membrane for 1 day. To obtain the CNDs dispersion with little impurity, such dialysis process was performed for another four times with changing water every half of day. The resultant CNDs (designated as CNDs-D) were dispersed in water for further characterization and use.

CNDs were also prepared by microwave heating DIA solution in the presence of CSA, HNO_3 and HCl (designated as CNDs-S, CNDs-N and CNDs-C, respectively). Furthermore, CNDs were also prepared by microwave heating EA and TPA solution in the presence of H_2SO_4 (designated as CNDs-E, and CNDs-T, respectively).

Detection of H_2O_2

For detection of H_2O_2, kinetic measurements were carried out by monitoring the absorbance change at 653 nm. In a typical run, 50 μL of CND_S dispersion was added into 800 μL of NaAc buffer solution (pH: 4.0), followed by adding 200 μL of TMB solution (1 mM in ethanol). After that, 5 μL of H_2O_2 was added into the mixture. The UV-vis spectra were recorded after reaction for 20 min at 35 ºC.

Detection of glucose

Glucose detection was performed as follows: 1) 100 μL of 1 mg/mL GOD and

100 μL of glucose of different concentrations in 200 μL of 10 mM Na_2HPO_4 buffer (pH 7.0) were incubated at 37 °C for 60 min; 2) 200 μL of TMB (1 mM in ethanol), 50 μL of CNDs dispersion, and 800 μL of NaAc solution were added into above glucose reaction solution; and 3) the mixed solution was incubated at 35 °C for 120 min and then for standard curve measurement.

Quantum Yield Measurements

Quantum yield was measured according to established procedure (Lakowicz, J. R. *rinciples of Fluorescence Spectroscopy*, 2nd Ed., **1999**, Kluwer Academic/Plenum Publishers, New York). The optical densities were measured on UV-vis spectra were obtained on a UV5800 Spectrophotometer. Quinine sulfate in 0.1 M H_2SO_4 (literature quantum yield 0.54 at 360 nm) was chose as a standard. Absolute values are calculated using the standard reference sample that has a fixed and known fluorescence quantum yield value, according to the following equation:

$$\varphi_x = \varphi_{std} \frac{I_x}{A_x} \frac{A_{std}}{I_{std}} \frac{\eta^2{}_x}{\eta^2{}_{std}}$$

Where φ is the quantum yield, I is the measured integrated emission intensity, and A is the optical density, and η is the refractive index. The subscript “std” refers to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects absorbencies in the 10 mm fluorescence cuvette were kept under 0.1 at the excitation wavelength (360 nm).

Table S1 A comparison with other colorimetric glucose detection systems based on nanostructures.

Catalysts	Detection limit (μM)	Linear detection range (μM)	References
Graphene oxide	1	1-20	11b
Au nanoparticles	4	18-1100	11c
CDs	0.4	1-500	11d
Fe_3O_4 nanoparticles	30	50-1000	11g
CNDs	0.5	1-10	This work

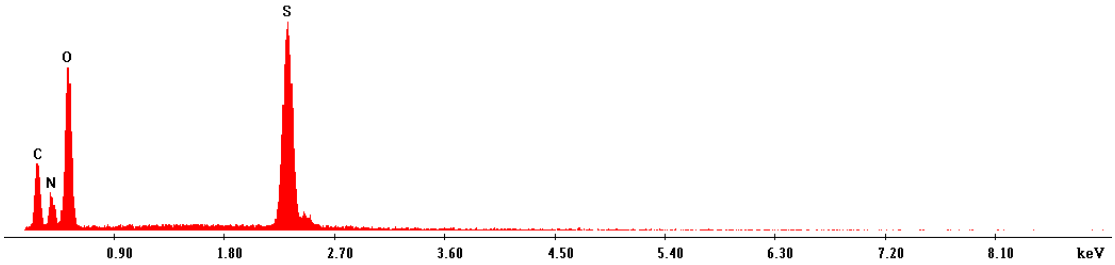

Fig. S1 EDS spectrum of CNDs-D thus obtained.

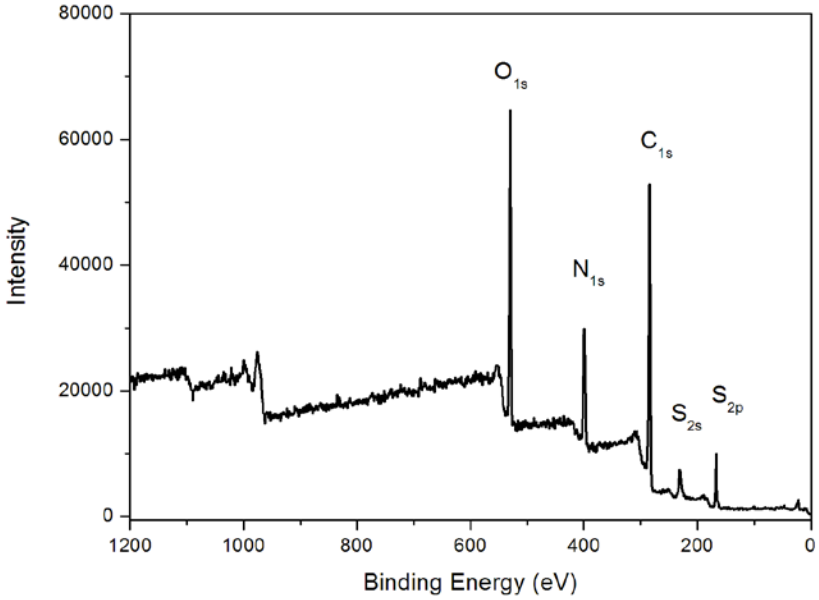

Fig. S2 XPS spectrum of CNDs-D thus obtained.

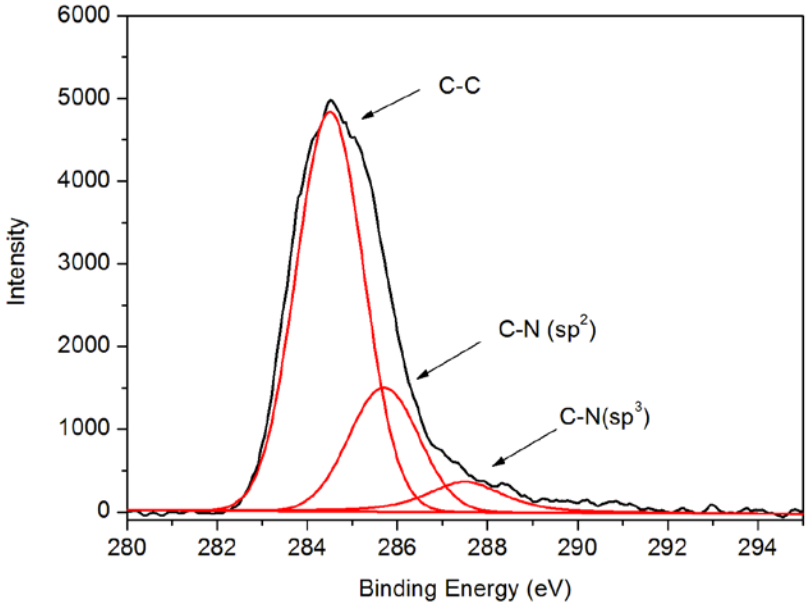

Fig. S3 C_{1s} spectrum of CNDs-D thus obtained.

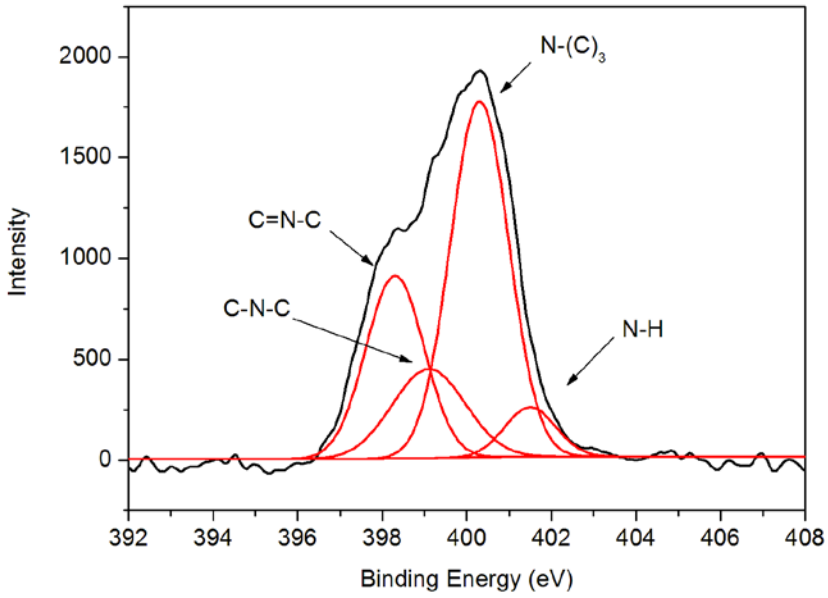

Fig. S4 N_{1s} spectrum of CNDs-D thus obtained.

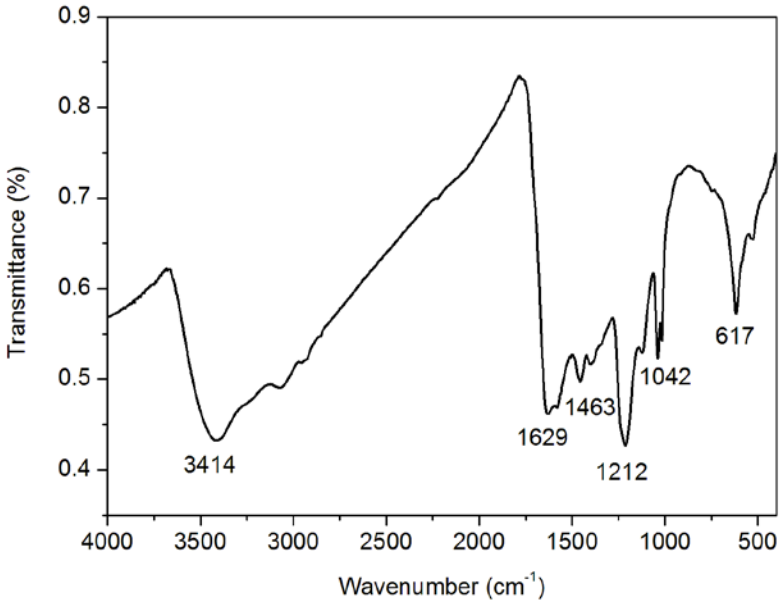

Fig. S5 FT-IR spectrum of CNDs-D thus obtained.

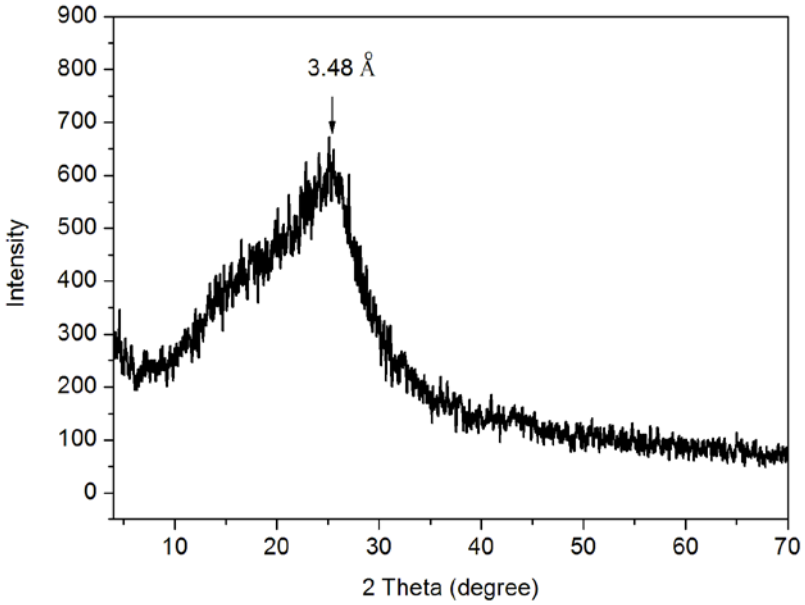

Fig. S6 XRD pattern of CNDs-D thus obtained.

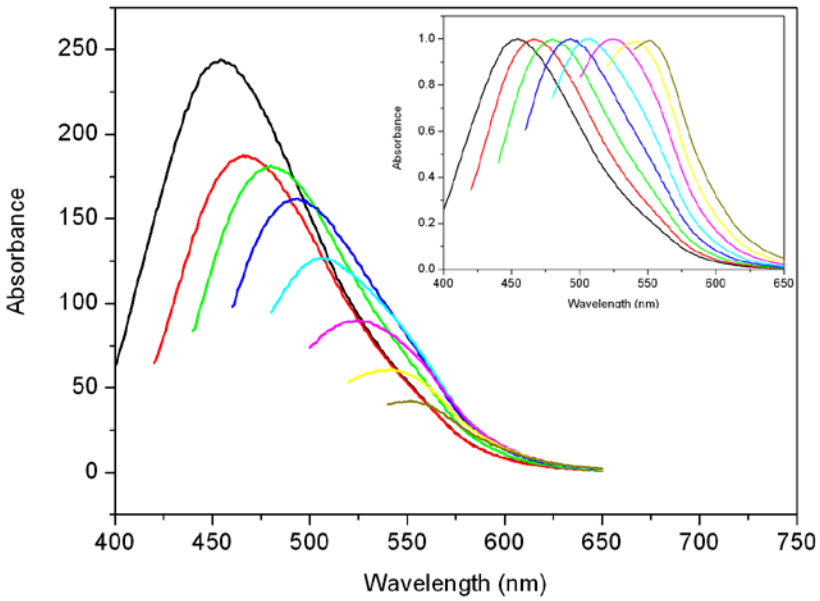

Fig. S7 PL emission spectra (with progressively longer excitation wavelengths from 380 nm to 520 nm on the left in 20 nm increment) of the CNDs-D dispersion. Inset: The normalized PL emission spectra.

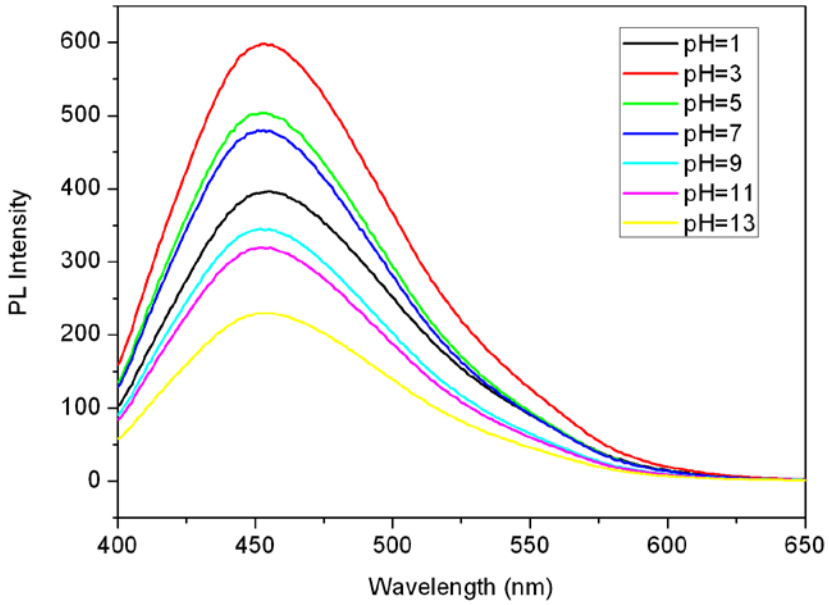

Fig. S8 The effect of the solution pH value on CNDs-D fluorescence.

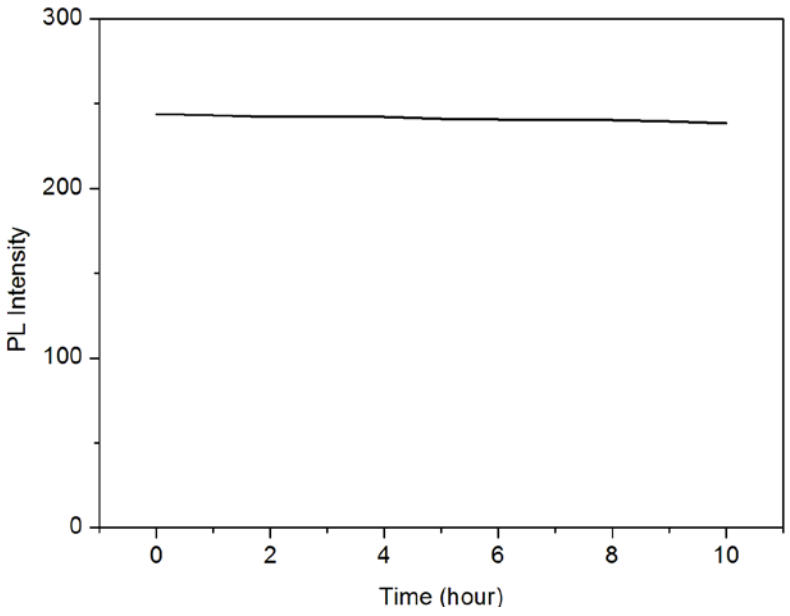

Fig. S9 Emission intensity of CNDs-D during continuous excitation at 365 nm.

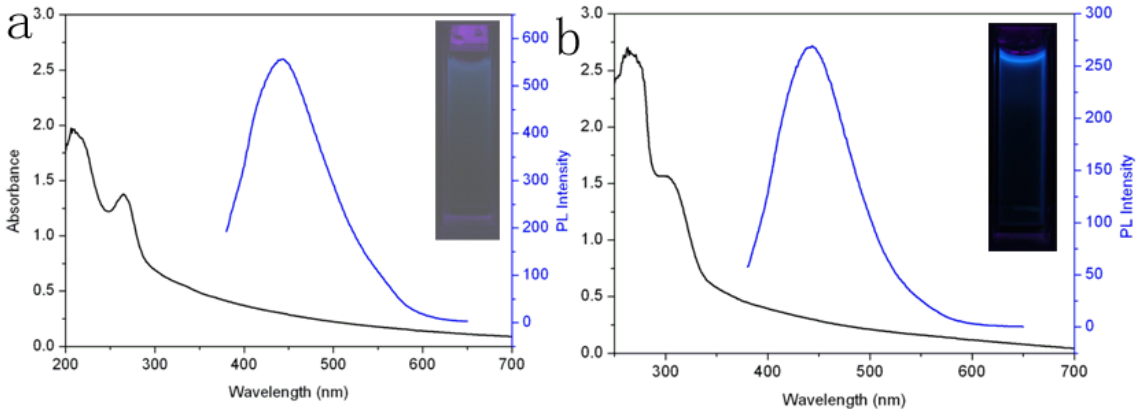

Fig. S10 UV-vis absorption and PL emission spectra of (a) CNDs-E and (b) CNDs-T, respectively. Inset: the corresponding photographs in water under UV light (365 nm).

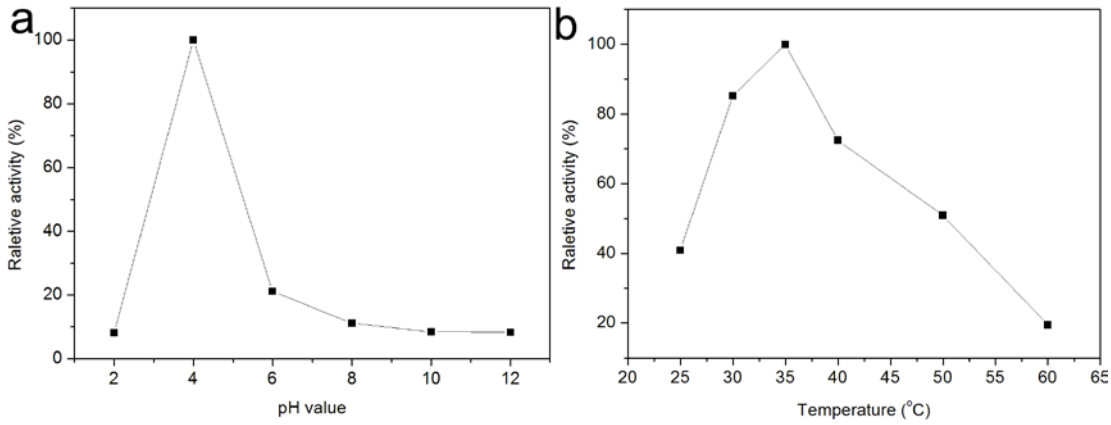

Fig. S11 The effect of pH value (a) and temperature (b) on the catalytic activity of CNDs-D.